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16. ABSTRACT

Systematic analysis of organic pollutants began a quarter century ago with the decision to apply current methods of organic qualitative analysis to multigram amounts of mixed organic pollutants recovered from extremely large sample volumes, by carbon adsorption or liquid extraction. The available tools (classical organic chemical analysis, sensory methods, molecular complexes, X-ray diffraction, ultraviolet and infrared spectrometry, and primitive chromatography). These tools accomplished some landmark achievements in abatement of organic chemical pollution of water supplies, including: the foundation of oil spill source detection by passive labeling, the analytical proof that forced the conversion of the detergent industry to biodegradable products, the first discovery of unforeseen pollution by chlorinated pesticides, and the first animal studies of carcinogenicity of organic water contaminants.

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CHAPTER 1

THE FOUNDATIONS OF ORGANIC POLLUTANT ANALYSIS

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The timing of this book is remarkably significant since it marks the 25th anniversary of a landmark development in the analysis of organic pollutants in the environment. The event commemorated is the introduction in 1950 by Braus, Middleton and Walton[1] of large-scale sampling of organic pollutants, thus making possible the application of the entire range of available methodology for systematic analysis.

APPLICATION OF SYSTEMATIC ORGANIC ANALYSIS

At the beginning of this 25-year period of progress, available methods for analysis of organic pollutants in water were embodied in the ninth edition of *Standard Methods*.[2] On the whole, organics could be measured either directly as a general aggregate (BOD and COD) or indirectly (odor, color). There were a few methods for specific organic substances in waters or wastes: oil, grease, organic nitrogen, cyanide, tannin-and-lignin, phenol, and furfural. There was already a method, though based on an impractical wet oxidation procedure, for total organic carbon, thus anticipating a major later instrumental development. There were a few unusual methods, *e.g.*, albuminoid nitrogen and methane, which are rarely used today.

In 1950 the methodology for organic chemicals in air pollution was even more primitive. No reference comparable to *Standard Methods* existed. The current emphasis was on determining the concentration of total particulates and total soluble organic particulate matter. There was a method for trapping automobile exhaust gases and determining aldehydes in the condensate. At the same time there were some early experiments

on applying long-path infrared analysis to detect hydrocarbons in ambient air. For several years progress in the air pollution field was made by borrowing methodology developed in water pollution research.[3]

New Direction in Sampling

In 1950 laboratory practices in qualitative organic analysis largely followed the system in the third edition of the manual by Shriner and Fuson.[4] The principal features of this system were: determination of solubility classes, application of classification tests (for functional groups and structural characteristics), and preparation of derivatives. The authors recognized that "It is very rarely possible to identify the constituents of a mixture without previous separation." In their system, separation of mixtures was based on chemical character, *i.e.*, differences in polar character affecting solubility in water and organic solvents.

The difficulty in applying the Shriner and Fuson system to water pollution analysis lay in the need for relatively massive organic samples, free of water. For example, the instructions for separation of mixtures begin: "From 25 to 50 g of the mixture is mixed with 75 ml of ether . . ." Typical weights of isolated organics for classification tests are 0.1 g (solids) to 2 ml (liquids), and for derivative preparation, 0.3 g solids to 1.0 g liquids. Even if the practical semimicro techniques of that time were substituted in the system, requirements for each test would be 0.025 to 0.10 g of each organic compound.

Braus and his co-workers decided in 1950 that it was no longer practical to base organic pollutant analysis on attempts to develop a catalog of ultrasensitive analyses for specific organics in water samples of convenient size for laboratory processing. It was obvious that an entirely different sampling approach had to be devised to supply the comparatively massive organic samples required for systematic separation and identification. The solution was to filter 5000 gallons (sometimes more) of water through a column of activated carbon. The organic pollutants were adsorbed upon the carbon, which was then air-dried and exhaustively extracted with ether. The yield of water-free organic mixture was 2-5 g, typically about 4 g. For enhanced safety, chloroform replaced ether as the extraction solvent (chloroform was not then recognized as a possible carcinogen). Later a second extraction with ethanol was added, yielding an additional 2-10 g of organic sample.[5] Carbon adsorption sampling was extended with partial success to organics in airport atmospheres,[6] and currently with great success to industrial atmospheres.

Even 5000 gallons of water sometimes yielded a sample of organic pollutants that was too small to allow extensive analysis. The carbon

filter sampling system, both the filter array and the extraction apparatus, was scaled up 80-fold.[7] By this means, chloroform extracts weighing 150-1700 g ("megasamples") were obtained, allowing for much more extensive analyses. It is noteworthy that the recent discovery of a large number of organic pollutants in the New Orleans drinking water was made using organic extract samples obtained by use of the same apparatus.[8]

Specialized Analytical Methods

A respectable array of specialized methods and instruments for organic analysis was available in 1950. The best catalog of these was assembled by Weissberger.[9] They became useful in analysis of organic environmental pollution only after the carbon filter sampling method came into use, since they were best applied to isolated pure compounds and their derivatives. Some of the available methods were: chemical microscopy, X-ray diffraction, ultraviolet spectrometry, polarography, radioactive labeling (isotope dilution methods), and molecular complexes, *e.g.*, inclusion compounds. Mass spectrometry was already in use in the analysis of petroleum components, but the method was first applied to water pollution in 1953.[10]

Three methods were in the analyst's armament in 1950 that later made especially important contributions to water pollution research. Infrared spectrometry has the special virtue of being applicable to impure organic samples and even to mixtures. Its use with water pollutants began almost simultaneously with the development of carbon filter sampling. Many forms of chromatography—column adsorption and partition, paper, electro- and thin-layer—were already in common use and awaited only the availability of suitable isolates of organic pollutants. Sensory methods—measurement of odor and taste—can be considered a specialized form of bioassay, probably the most sensitive. They are applicable to water samples and thus were used importantly even before the improved sampling method.

This paper presents examples of the progress made in the past 25 years by the timely application of currently available analytical methods. During this period there were two major scientific advances relevant to water pollution. One was the improvement and expansion of methods to assess the health effects of pollutants, particularly carcinogens. As a result, investigations of organic pollutants in water received new legal, organizational and budgetary support. The other was the continuous development of gas chromatography, a technique that provided a quantum increase in the ability to separate organic mixtures (replacing distillation systems that were never truly effective). At the same time, gas chromatography

yielded data for pollutant identification—retention time (analogous to boiling point of a pure component) and specific detector response (analogous to elemental and functional group determination).

PROGRESS IN ORGANIC POLLUTANT ANALYSIS

During the 25-year period reviewed here, the most productive advances initially involved improvement in the new sampling method and expansion in the application of conventional systematic organic analysis and related specialized instrumental methods.

Adsorption on activated carbon is a complex phenomenon still not well understood. It was recognized from the start that the carbon itself is a major variable. Braus *et al.*[1] showed that a carbon manufactured specifically for water treatment was nearly five times as effective as another type of carbon. Later work considered the effect of pore size, pore volume, and surface functional groups on adsorption capacity, but showed that there is little difference in adsorption activity between a number of brands of carbon expressly developed for water purification. However, carbons varied several-fold in their content of extractable organic matter and a brand with a consistently low blank became the standard method material. The effectiveness of different solvents in desorbing organic material from carbon also varies notably.[11] It was shown that consecutive extraction with chloroform and ethanol, later established as the standard method, was only slightly less effective than the most active combination of six solvents studied.

Experiments with a number of pure organic compounds in dilute solution showed that their adsorption in a carbon filter was 91-100% complete, but solvent extraction usually desorbed only 70-85% of the adsorbed compound.[12] At the time many conjectured that the loss was due to decomposition catalyzed by the active carbon surface. However, a definitive study of the adsorption-desorption of phenol labeled with carbon-14 showed that the unrecovered phenol remained, trapped but unchanged, in the pores of the activated carbon.[13]

Another advance was based on the carbon-14 label in organic pollutants. Since industrial chemical wastes are derived from fossil sources, they contain no radioactive carbon, whereas organics derived from sewage and run-off from vegetated land will have nearly a contemporary level of radioactivity. Accordingly, an assay for carbon-14 can reveal the relative organic pollution contributions of these two principal classes of sources.[14] This work also showed that the industrial pollutants predominate in the chloroform extract while natural and municipal pollutants largely make up the ethanol extract. Accordingly, the yield of chloroform extract is

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an approximate measure of industrial pollutants, many of which are known to pose health risks. This rationale led to the adoption of a limit on concentration of CCE (carbon chloroform extract) in drinking water as a practical means to avert the health hazard of countless unknown industrial organic pollutants.[15] This same concept was later adopted as the European and International drinking water standards.

The superscale carbon filter system (Megasampler)[9] has been mentioned previously. Besides providing more abundant samples for expanded analysis, the system made available sufficient organic material for long-term animal testing of adverse health effects. The result of these tests was the first demonstration, in 1963, of carcinogenicity in the organic pollutants of a public drinking water supply.[16] By 1969, the apparent carcinogen in that water supply was identified as *bis*-(2-chloroethyl)-ether, and its tumor-producing activity was demonstrated.[17]

Other methods of concentrating organic pollutants from water were developed. Some of these were: liquid-liquid extraction (including variations to handle 500-gallon or larger samples), adsorption on polyurethane foam or polymer beads, collection on macroreticular ion-exchange resins, and volatilization with subsequent trapping in solvents or on adsorbents. Many chapters presented in this book illustrate applications of these sampling methods.

Group Separation Methods

The availability of carbon filter extracts made possible the application of the solubility-group separation system of Shriner and Fuson, yielding initially these groups of related organic pollutants: amphoteric, basic, acidic, phenolic, and neutral compounds.[1] Experience in use of the method resulted in dropping the amphoteric group and adding a water-soluble group.

The neutral group thus separated is quite heterogeneous. In addition to aliphatic and aromatic hydrocarbons, it contains a variety of functional group classes, *e.g.*, chlorinated hydrocarbons, alcohols, esters, and aldehydes and ketones. Adding a step to isolate carbonyl compounds by dissolving them in sodium bisulfite solution or combining with Girard's or other carbonyl reagents provided little new analytical information. The same fact was true when efforts were made to treat esters and a distinct group. On the other hand, complex formation served very effectively to separate and classify neutral hydrocarbons, until gas chromatography came into use. Normal aliphatic hydrocarbons were precipitated as their urea complexes, regenerated and recovered, thus providing convincing evidence of the presence of petroleum materials. Polycyclic aromatic hydrocarbons

were precipitated as their complexes with 2,4,7-trinitrofluorenone. Inadequate tools for characterizing the isolated aromatic hydrocarbons were then available, but an indication of 1,2'-dinaphthyl was observed.[18] This complexing agent is currently being revived with the new attention being given to carcinogenic aromatic hydrocarbons in the environment.

Column adsorption chromatography was developed as a more useful means to subdivide the neutral group into fractions designated as aliphatics, aromatics, and oxygenated compounds. The aliphatic and aromatic fractions of petroleum pollutants gave characteristic infrared spectra more recognizable than the spectra of the weathered total oil. The method, which is the basis of many current oil spill investigation methods, was applied in 1955 to detect the presence of petroleum refinery wastes[19] and in 1959 to the identification of the sources of oil slicks in the Santa Barbara channel.[20] This latter application startlingly foresaw the oil spill problems that were to erupt a decade later.

The chromatographic separation of neutrals is an effective way to concentrate the polycyclic aromatic hydrocarbons in environmental samples for detailed analysis. It is widely used for this purpose in air pollution research.[21]

Most chlorinated hydrocarbon pesticides concentrate in the aromatic fraction, where they can be detected by infrared spectrometry. This property made possible the early successes in monitoring insecticides as unsuspected pollutants in environmental samples.[22]

Application of Instrumental Analyses

Infrared spectrometry was applied to carbon filter samples almost from the start of the filter method. The infrared technique can be applied to mixtures and impure compounds; thus, it was very informative with the still-complex fractions of organics obtained by group separation. Some noteworthy firsts in organic pollutant analysis were accomplished by infrared spectrometry. The detection of chlorinated pesticides has been described. The definitive identification of synthetic detergents (alkylbenzene sulfonates) as the cause of severe foam problems in streams, water supplies, and sewage treatment plants was also accomplished by infrared spectrometry.[23] This proof resulted in the redirection of the entire detergent industry to the manufacture of biodegradable products.

The discovery of *o*-nitrochlorobenzene as a Mississippi River pollutant was made in 1958 through interpretation of its infrared spectrum in carbon filter extracts[24]; the spectrum was especially clear in the aromatic fraction. This compound was traced for a thousand river miles from an industrial waste source in St. Louis to the water supply intake at New

Orleans, where its concentration was estimated at 2 μg/l. This was the first of the potentially health-threatening organic pollutants to be discovered at New Orleans, anticipating the endrin pollution discovered in 1963 and the many recently discovered toxic organics demanding concentrated attention at the present time.

Infrared spectrometry was applied, without requiring carbon filter sampling, to an unusual, unpublished case of organic pollution of ground water. The pollutant was an organic phosphorus compound produced by deactivation of nerve gas at a military facility. The aquifer was affected by infiltration from a waste lagoon. In this case, chemical analysis had an unexpected consequence—earthquakes resulted when authorities ordered the waste thenceforth to be disposed of by deep-well injection.

Ultraviolet spectrometry is so powerful a tool that it has to be valuable in many ways in environmental research. An early application was to determine phenols in aqueous wastes and polluted waters.[25] This tool has been especially productive, combined with adsorption chromatography, in the identification and determination of carcinogenic aromatic hydrocarbons in both atmospheric and aquatic environments.[26]

Wherever the classical system of organic analysis calls for the preparation of a solid derivative and identification by its melting point, X-ray diffraction provides much surer identification. There have been only a few applications to water pollution research. One of these was the identification of pyridine bases in drinking water derived from an aquifer contaminated by an industrial waste lagoon. The mixture of bases was precipitated as their corresponding chloroplatinates, which were readily identified and estimated from their X-ray diffraction patterns.[27] X-Ray diffraction can be applied to all solid pollutants or pollutant derivatives, *e.g.*, fatty acids as their silver salts by use of available semimicro specimen preparation procedures.

The word "chromatography" refers to an exceedingly broad array of separation methods, a fact that was equally true before gas chromatography came into general use. A few applications of other types of chromatography are sketched briefly here. In unpublished work in the early 1950s, paper chromatography was used to identify phenols as their azo dyes in industrial wastes. It was often possible to determine if cases of phenolic pollution of streams were caused by steel mills (coke ovens) or petroleum refineries because the phenols in their wastes produce characteristic paper chromatograms.

Column partition chromatography has been successfully applied to separate, identify, and measure organic acids in sewage.[28] Several applications of column adsorption chromatography have been described. This method and its analog, thin-layer adsorption chromatography, are favored

means for clean-up and separation of chlorinated pesticides for identification and analysis, *e.g.*, by infrared spectrometry.[29] High-performance liquid chromatography, though a relatively recent development, is now broadly applied to environmental problems. It may be the only technique to approach the problem of analyzing the estimated 90% of organic materials in water that are nonvolatile. The first such application, in 1972, separated 77 compounds from a primary sewage, of which 13 were identified.[30]

Sensory Methods

Systematic analysis of organic pollutants began 25 years ago as a campaign against taste and odor problems. These sensory properties are the most readily evident and effectively measurable kinds of biological effects. As a first step, the procedure for measuring sensory contribution through the threshold test was made consistent with modern panel test procedures, in the form which now appears in *Standard Methods.* As the analysis of pollutants advanced, it became evident that odors are often caused by the presence of more than one odorous organic substance. The question arose: how do such odorant mixtures affect the threshold test? Psychologists had conducted primitive investigations of this question as far back as 1917. New studies reported in 1962 showed definitively that mixed odors are usually additive at the threshold level and some mixtures are even synergistic.[31] These observations supported the experimental evidence that the same phenomena operate in waters containing more than one odorous pollutant.

Measurement of odor and taste and distinguishing between them was the basis of a fundamental study on the intense odor generated by chlorination of phenols. The nature of the odorous products has long been a mystery. The odor depends on the chlorine:phenol ratio. At the optimum ratio the odor is contributed by three distinct chlorophenols, each of which was identified by one or more of these methods: paper chromatography, infrared spectrometry, or derivative formation.[32]

CONTRIBUTIONS OF GAS CHROMATOGRAPHY

Gas chromatography is a phenomenally powerful separation system resembling fractional distillation, but it is capable of separating 50 or 100 components in a 1-mg or 2-mg sample. In comparison, earlier efforts at refining the group separation system by adding microdistillation steps were hopelessly ineffective. As gas chromatography was being developed, there were many unpublished efforts to apply it to analysis of air

pollutants and water pollutants, probably in that order. Sometime between 1960 and 1963 the analysis of chlorinated pesticides in water by gas chromatography was demonstrated, using the primitive columns and detections of that time. In 1963 a report of pollution of the water supply at Hawaii Volcanoes National Park revealed that chlordane was discovered in the water and identified by gas chromatography.

The rapid introduction of new specific detectors in effect added the simultaneous capability for functional group detection to the separating power of gas chromatography. For example, electron capture and coulometric detectors were almost specific, with appropriate precautions, for chlorinated pesticides and polychlorinated biphenyls. Flame photometric detectors were used with similar specificity for phosphorus pesticides in one mode, for alkyl mercury compounds in a second mode, and for identification of petroleum pollutant sources through characteristic patterns of sulfur compounds in a third mode.[33]

The analogy between gas chromatography and fractional distillation has been drawn. Using slightly larger samples with preparative columns, the separated pollutant compounds are isolated and recovered, making them available for all the analytical procedures already enumerated: infrared spectrometry and sensory testing. By this combination, 11 organic compounds, originating in petrochemical wastes, were identified in 1961, in the Kanawha River, a tributary of the Ohio River. Their individual and collective contributions to the river odor problem were determined,[34] resulting in the first state regulation of a group of specific organic waste compounds. Interestingly, ten of the same compounds were found two years later in Ohio River water at Cincinnati, and the next year four of the same compounds were identified at Cairo, Illinois, hundreds of miles downstream.

Preparative gas chromatography was used to solve a problem of many decades, the identity of the pollutant causing earthy-musty odors in water supplies in many areas of the world. The responsible microbiological metabolite, *geosmin*, was trapped in sufficient quantity to permit its structural determination by mass spectrometry, infrared and nuclear magnetic resonance spectroscopy and synthesis.[35]

The application of mass spectrometry to identify geosmin, a gas chromatography isolate, anticipated today's most powerful analytical system, coupled gas chromatography–mass spectrometry–computerized data interpretation. The importance of this combination is apparent from its dominance in the following chapters of this book.

FUTURE PROSPECTS

This chapter is intended as a retrospective view of the development of systematic analyses of organic pollutants in the environment. It is appropriate to use this review as a base from which to anticipate the directions of future progress. It is obvious that gas chromatography and its coupling with mass spectrometry are today's principal thrust. But it is important not to fall into the "black box" trap—to concentrate effort where a convenient instrument with computerized output is easily available. We must consider that work to date has dealt almost exclusively with the 10% or less of organic pollutants that are volatile. New methods and instruments will be needed to analyze the nonvolatile remainder for which gas chromatography is inappropriate. Liquid chromatography and pyrolysis-gas chromatography (including "carbon-skeleton" analysis) come to mind first as possible tools.

Both analysts and program managers should reconsider the principles underlying all the progress that has already been made in environmental analysis. One of these was the wise application of the large body of chemical science. The environmental field needs the resurgence of contributions of soundly-trained chemists, not merely instrument specialists, although chemistry will lead to contributions from new or little-used instruments, such as carbon-13 magnetic resonance.

The other principle is wide-open programming. Past progress was made in unexpected directions through allowance for the exercise of creativity. Most of the toxic pollutants now sought to be controlled by regulation were discovered while pursuing more general scientific objectives. Many of the most productive methods resulted from the search for taste or odor causes. Yet today most of the emphasis and virtually all the support is given to research on known "health-related" pollutants. "Esthetic" pollution effects are severely downgraded. Research programs should provide for a wider range of basic scientific interest. In the future, as in the past, environmental programs should allow for the exercise of creativity and the serendipitous fallout from programs of broad scope.

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